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THE MOLECULAR STRUCTURE OF PYRAZINE AS DETERMINED FROM GAS-PHASE ELECTRON DIFFRACTION DATA*

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ABSTRACT

The structure of pyrazine (1,4 diazabenzene, $C_4H_4N_2$) has been determined at 333 K by means of gas-phase electron diffraction. The r_g parameters are as follows: r(C—C) = 1.339 ± 0.002 Å, r(C—N) = 1.403 ± 0.004 Å, r(C—H) = 1.115 ± 0.004 Å, ∠C—C—N = 115.6 ± 0.4°, and ∠C—C—H = 123.9 ± 0.6° (error limits are 2.5σ). At a 10% level the r_α structure does not differ significantly from the structure in the solid state, so long as high order X-ray results corrected for librational motion are used; otherwise significantly different results are found even at the 1% level. Calculated and observed mean square amplitudes compare favourably.

INTRODUCTION

The crystal structure of pyrazine was determined in 1957 by Wheatley [1] and has been redetermined recently [2]. The molecular structure in the gas phase was investigated in 1939 by Schomaker and Pauling [3]; the accuracy of the latter data is below present standards. In order to obtain gas-phase structural data suitable for comparison with the structure in the solid state, the present reinvestigation was carried out.

EXPERIMENTAL

Commercially available pyrazine (Merck, purity 99%) was dissolved in ether and dried over molecular sieves (Merck 4 Å pores) for 24 h. After filtration and evaporation of the solvent, vacuum sublimation was carried out. The purity of the sample was estimated to be at least 99.9%.

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TABLE 1

Pyrazine: gas-phase electron diffraction experiments

Distance (mm)	Number of plates	s-Range[a]	Number of data points
590	3	3.00—12.00	37
340	3	5.75—20.75	61
200	3	8.25—29.75	87
Sample temperature: 40°C			
Nozzle temperature: 60°C			

[a] $\Delta s = 0.25$ Å^{-1}.

Sectored electron diffraction patterns were recorded on Kodak electron image plates with Balzer's KD-G2 Eldigraph [4] at nozzle-to-plate distances of approximately 190, 340 and 590 mm (see Table 1). Modifications to the diffraction unit have been described elsewhere [5]. All plates were photometered with a modified double-beam Joyce—Loeble microdensitometer. During each scan the plate was oscillated over an angle of 30°. Density values were taken at 0.2 mm intervals. Smoothed optical densities were converted to intensities at intervals of 0.25 Å^{-1} according to the one-hit model of Forster [6].

Preliminary wavelength calibration was done with thallium(I) chloride (a = 3.8414 Å [7]) resulting in a wavelength of 0.06162 Å at 40 kV. However, calibration against a gaseous sample is to be preferred [8]; therefore, using the same experimental settings, the diffraction patterns of benzene were also recorded (see Table 4).

DATA TREATMENT

The data were corrected and processed in the usual way [5, 9]. Intensities were levelled by the theoretical atomic intensities. Inelastic scattering functions were taken from the tables of Tavard et al. [10]. Elastic scattering factors were calculated by the partial wave shift program devised by Peacher and Wills [11]. Hartree—Fock potentials [12] were used.

A starting model (Fig. 1) was constructed from pyrazine X-ray positional parameters [2] and benzene vibrational parameters [13] assuming D_{2h} symmetry [14]. A preliminary experimental background was found by smoothing the correlation background using spline functions [15]. Long wave errors

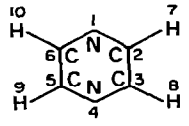

Fig. 1. Atomic numbering in pyrazine.

in the background were corrected by inverse-Fourier sine transformation of the experimental radial distribution function (RDF) for $r < 0.8$ Å. The experimental RDF was calculated using theoretical $sM(s)$ data in the range $s = 0.0$ to $s = 3.0$ Å^{-1}, together with experimental data beyond $s = 3.0$ Å^{-1}, blended smoothly together in the regions of overlap. A diagonal weighting scheme with weights proportional to s was used in the least-squares parameter fit of the levelled intensities to match $1 + RM(s)$. The data of the three camera distances were entered as independent data sets.*

Depending on the number of u-parameters varied, two solutions were found (Table 2). Note that some u-parameters were constrained to be equal. An asymmetry constant $\kappa = 10^{-5}$ Å^3 was assigned to the C—H bond. In model 1, the non-bonded C···H and N···H amplitudes were fixed to the calculated values (see next section).

According to the Hamilton R-test [16] model 2 (14 parameters) did not give a better description than model 1 (12 parameters) at the 5% level. Levelled intensities and final background curves are given in Fig. 2. Figure 3 shows the final RDF. For model 1 the resulting r_g parameters are shown in Table 2. The correlation matrix associated with model 1 is given in Table 3.

The data for benzene were processed analogously, and information on the benzene experiment is given in Table 4. From the results obtained, it appeared that the wavelength as calculated from the TlCl data was underestimated by 2.5‰ assuming the benzene C—C r_a distance to be 1.3979 Å [17]. The uncertainty in the refined C—C bondlength was 0.4‰. Hence the wavelength used was 0.06177 ± 0.00003 Å. The results for pyrazine were corrected accordingly.

VIBRATIONAL CORRECTIONS

In order to obtain a geometrically consistent r_α structure, $r_a - r_\alpha$ corrections were calculated according to $r_a - r_\alpha \simeq K - u^2/r$ [18]. For the calculations the program NCTB [19] was used. Valence Force Field (VFF) data for the in-plane vibrations were taken from the work of Scrocco et al. [20]. The VFF elements for the out-of-plane vibrations were estimated by taking data refined for p-dichlorobenzene [21]. The resulting amplitudes are given in Table 2 together with the $r_a - r_\alpha$ corrections.

DISCUSSION

Refined u-values of model 1 compare favourably with those calculated. The largest discrepancy for bonded distances ($\sim 2.5\sigma$) is found for the u(C—H) value.

The principal difference between the geometry of the two models is in the

*A list of intensities has been deposited with the British Library Lending Division as Sup. Pub. No. SUP 26073 (4 pages).

TABLE 2

Pyrazine: molecular structure and vibrational parameters (distances and u-values in Å, angles in degrees)

Parameter	r_g (Model 1)[e]	Parameter[b] number	X-ray [2]	r_α (Model 1)[a]	r_α (Model 2)[a]
r(C—N)	1.339(2)	1	1.3392(18)	1.3367(16)	1.3369(16)
r(C—C)	1.403(4)	2	1.3931(26)	1.3999(43)	1.3983(44)
r(C—H)	1.115(4)	3	1.08 (1)	1.0989(44)	1.0936(46)
∠(C—N—C)	115.6 (4)	4	116.31 (14)	115.64 (37)	115.41 (33)
∠(C—C—H)	123.9 (6)	5	122.2 (2.1)	123.87 (58)	116.3 (4.0)
	$r_a - r_\alpha$	Parameter number	u(calc.)	u	u
C—N(1—2)[d]	0.0011	6	0.044	0.046(2)	0.047(2)
C—C(2—3)	0.0011	6	0.046	0.046(2)	0.047(2)
C—H(2—7)	0.0109	7	0.078	0.090(5)	0.091(2)
N··N(1—4)	—0.0008	8	0.059	0.073(8)	0.063(8)
C··N(2—4)	0.0000	9	0.054	0.061(3)	0.064(3)
C··N(2—6)	0.0001	9	0.053	0.061(3)	0.064(3)
C··C(2—5)	—0.0007	8	0.059	0.073(8)	0.063(8)
N··H(1—7)	0.0046	10	0.096	0.096	0.138(14)
N··H(1—8)	0.0025	10	0.096	0.096	0.138(14)
C··H(2—8)	0.0047	11	0.098	0.095	0.142(16)
C··H(6—7)	0.0031	11	0.094	0.095	0.142(16)
C··H(5—7)	0.0019	11	0.094	0.095	0.142(16)
H··H(7—8)	0.0021	—	0.156	0.156	0.156
H··H(7—10)	0.0042	—	0.129	0.129	0.129
H··H(7—9)	0.0030	—	0.118	0.118	0.118
Indices of resolution					
H = 590 mm		12		1.007(6)	1.009(6)
H = 340 mm		13		0.999(8)	1.003(8)
H = 200 mm		14		1.085(16)	1.092(16)
R_w[c]				2.969‰	2.881‰

[a] 2.5 × least-squares standard deviation given in parentheses; if not, the corresponding parameter is kept fixed. [b] Parameters with equal parameter number are constrained to be equal. [c] $R_w = [\Sigma w(M_{obs} - M_{calc})^2/\Sigma w(1 + M_{obs})^2]^{1/2}$. [d] For atomic numbering see Fig. 1. [e] r_g distances, r_α angles.

C—C—H angle: either 3.8° above or 3.7° below 120°. It will be noticed that in both cases the distribution of N··H and C··H distances is almost equal.

The five geometrical parameters of model 1 show a good agreement with the results obtained by X-ray diffraction of single crystals [2]. Following Hamilton [22] we calculated $M = \Sigma_{i=1}^{5} (\Delta_i/\sigma_i)^2$ and tested this quantity against $\chi^2_{5,0.10}$. Here $\Delta_i = P_i^{ED} - P_i^X$ and $\sigma_i = \{(\sigma_i^{ED})^2 + (\sigma_i^X)^2\}^{\frac{1}{2}}$, P_i and σ_i denote the parameter and standard deviation, respectively, of the electron diffraction (ED) and X-ray (X) experiments. For the electron diffraction parameters we choose r_α values rather than r_g values. The results are $M = 8.9$ for model 1 (and $M = 9.7$ for model 2). Since $\chi^2_{5,0.10} = 9.2$, we may accept the null-hypothesis, namely, that no difference exists between the parameters as determined by the two techniques (at the 10% significance level).

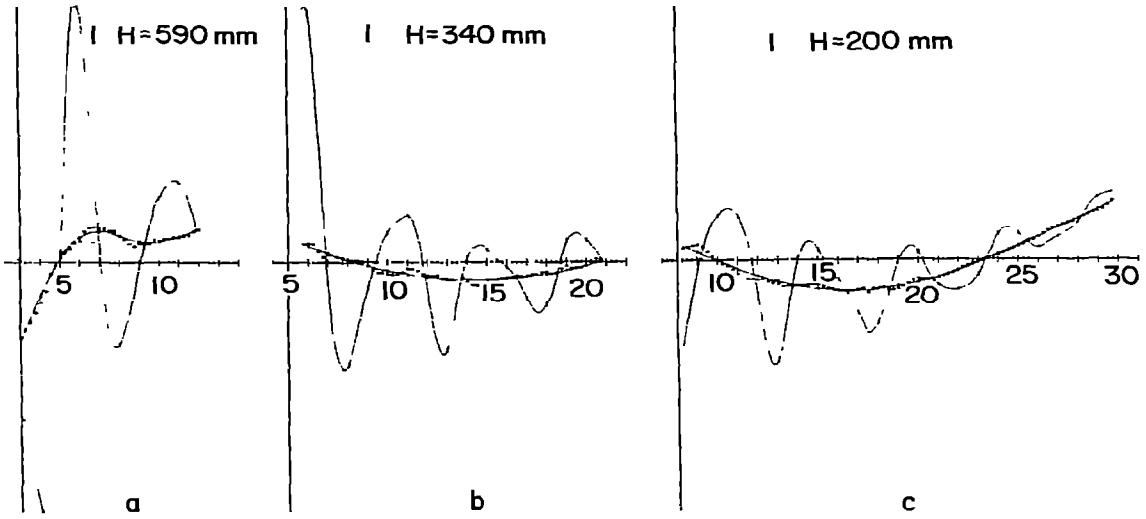

Fig. 2. Levelled intensity curves (—|—|—), empirical background (————), and correlation background (++++); (a) 590 mm, (b) 340 mm, and (c) 200 mm.

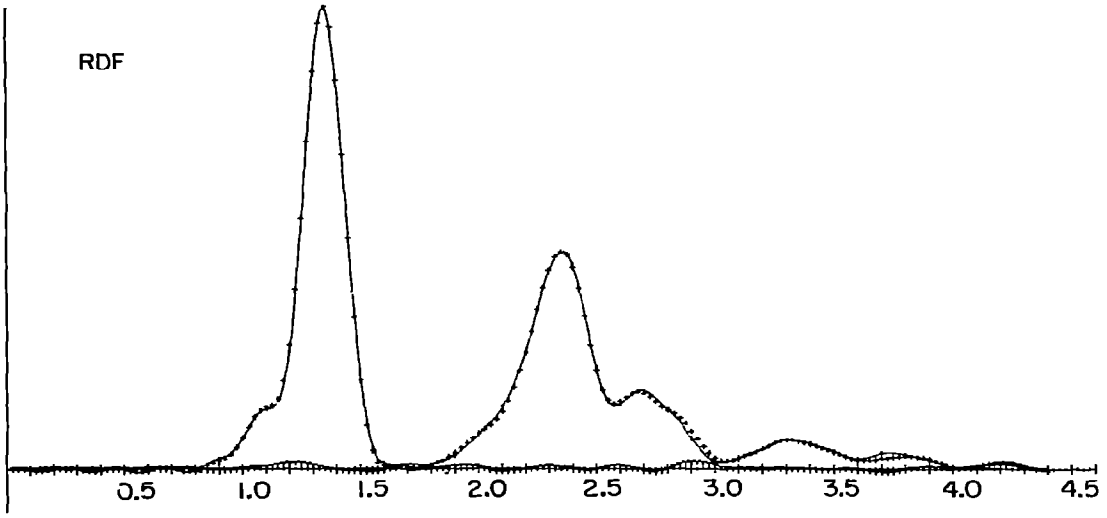

Fig. 3. Final RDF calculated using a damping of exp (—0.0015 s^2): theoretical RDF (———), experimental RDF (++++), and difference RDF (Y Y Y).

This result is not unexpected because pyrazine crystals are "van der Waals' " crystals, in which only weak intermolecular forces occur. However, it should be noticed that the X-ray parameters used are obtained from high order data and are corrected for librational motion. If no correction for librational motion is applied, the null hypothesis can be rejected even at the 1% level for parameters derived from high-order as well as full-angle data.

TABLE 3

Pyrazine: correlation matrix for model 1[a]

	1	2	3	4	5	6	7	8	9	12	13	14
1	100											
2	−94	100										
3	21	−14	100									
4	−67	72	−15	100								
5	37	−44	9	−14	100							
6	78	−81	−4	−60	39	100						
7	10	−19	−10	−15	13	21	100					
8	−31	34	−7	78	4	−28	−8	100				
9	−4	9	−1	64	31	0	−5	76	100			
12	9	−14	−59	−7	16	38	23	−1	9	100		
13	−3	2	−49	0	14	31	2	−2	12	47	100	
14	0	1	−24	0	−2	40	−4	6	12	35	47	100

[a]For numbering see Table 2.

TABLE 4

Benzene: experiments for wavelength calibration

Distance (mm)	Number of plates	s-Range[a]	Number of data points	Index of resolution
590	2	4.75—11.75	29	1.016(10)
340	1	5.25—20.75	63	1.038(11)
200	2	8.25—30.75	91	1.093(18)

Sample temperature: 22°C
Nozzle temperature : 60°C
R_w[b] : 4.806‰
κ(C—H) : 10.0×10^{-6} Å^3
κ(C—C) : 1.5×10^{-6} Å^3
u-values : refined

[a]$\Delta s = 0.25$ Å^{-1}. [b]For definition of R_w see Table 2.

The r_g structure of pyrazine is compared with those of benzene and pyridine in Table 5. The C—N bond lengths are equal within limits of error. The C—C bond lengths seem to be slightly larger than in benzene, whereas in pyridine they are virtually the same. In both pyrazine and pyridine the C—N—C angle and N—C—H angles are found to be smaller, and the N—C—C angle larger than 120° by a few degrees. The data in Table 5 also suggest that in pyrazine the C—H distance is somewhat larger than in benzene and pyridine, but part of the difference may be due to various systematic errors.

TABLE 5

Pyrazine: comparison[a] with pyridine and benzene

Benzene[b]	Pyridine[c]		Pyrazine[e]	
	r(C—N)	1.341(1)	r(C—N)	1.339(2)
r(C—C) 1.399(1)	$r(C_2—C_3)$	1.398(1)	r(C—C)	1.403(4)
	$r(C_3—C_4)$	1.396(1)		
r(C—H) 1.105(5)	$r(C_2—H_2)$[d]	1.107(2)	r(C—H)	1.115(4)
	$r(C_3—H_3)$	1.103(2)		
	$r(C_4—H_4)$	1.102(2)		
	∠(C—N—C)	117.0(1)	∠(C—N—C)	115.6(4)
	∠(N—C—C)	123.5(1)	∠(N—C—C)	122.2(4)
	∠(N—C—H)	116.0(1)	∠(N—C—H)	113.9(1.0)

[a]Distances in Å, angles in degrees. [b]r_g structure [13, 17]. [c]r_g structure, estimated from r_s structure [23] by adding perpendicular amplitude corrections K calculated for pyrazine. [d]From $r_g \approx r_0 + K + \langle \Delta r \rangle$, $\langle \Delta r \rangle$ = 0.018 Å (assumed). [e]Present study.

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